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(54) SUPERCOOLED METAL FOR ORNAMENTAL MATERIAL AND ALLOY FOR SUPERCOOLED METAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hard material for ornament having excellent glossiness and workability and further free from influence on the human body.

SOLUTION: This alloy is composed of Pt-Pd-Cu-P, in which the ratio of each component is controlled, by atom, to 5 to 70% Pt, 5 to 50% Pd, 5 to 50% Cu and 5 to 30% P, and the supercooled metal for an ornamental material is obtained by subjecting the above allay to dissolution and thereafter cooling the same at 101°C to 102°C.

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CLAIMS

[Claim(s)]

[Claim 1] With the alloy which consists of Pt-Pd-Cu-P, the percentage of each component is 5 <=Pt<=70at% and 5 <=Pd<=50at% and 5 <=Cu<=50at% and 5 <=P <=30at%, and after this alloy's dissolving, it is further. Supercooling metal for ornament ingredients characterized by being cooled by 101 degree-C/sec- 102 degree C/sec.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] When it uses for accessories, there is optimal hardness, and it is related with Pt system alloy ingredient which does not have effect on the body further.
[0002]
[Description of the Prior Art] It is observed in recent years as an ingredient in which unique properties -- a supercooling metal has hard hardness since it is not obtained by quenching a metal from a melting condition and is not crystallizing -- are shown.
[0003] Quenching making a supercooling metal generally has so far been considered as an indispensable condition. For example, it is made to fall after the copper water-cooled roll which carries out high-speed rotation of the molten metal, is made a thin foil-like tape and a thin flake, and the supercooling metal has been made.
[0004] everything but the supercooling metal alloy made by doing in this way recently -- bulk -- it has turned out that the supercooling metal of the shape of an ingot which is not a foil (the shape of an ingot) called as it is amorphous is made.
[0005] Making a cooling rate quick will change the cooling rate of a front face and the interior, if a configuration becomes large, and although a front face serves as a supercooling metal, the interior will have the usual metallic crystal. Therefore, in order to have cooled quickly until now, only the thing of the shape of a thin foil was able to be made.
[0006] However, though the supercooling metal of the shape of a recently comparatively big ingot (the shape of an ingot) is a comparatively late cooling rate, it has turned out by a certain kind of alloy presentation that it is possible.
[0007] However, the theoretical analysis why the combination of a presentation of these alloy elements becomes a supercooling metal has many still unknown points. Although some things (for example, that it is the alloy of what the interatomic distance left and P what makes a compound, and said phenomenon) are mentioned in phenomenon, it is not necessarily materialized as absolute rule conditions.
[0008] By the way, although noble metals, such as Au and Pt, were conventionally used as medical-application ingredients, such as charges of accessories material, such as a pendant, a ring, a broach, and a necklace, and dentistry, a catheter, since it was soft, these noble metals had the problem of being easy to attach a crack by friction at the time of use. Although the method of increasing hardness by carrying out little addition of other metals, and considering as an alloy at noble metals, such as Au and Pt, was generally used in order to solve this problem, it was not sufficiently satisfactory in respect of hardness etc. as such an alloy.
[0009] Moreover, for the supercooling metal of the shape of an ingot reported recently although the idea of using the above supercooling metals as an ingredient of such accessories has also gone up (the shape of an ingot), the most is a component. When nickel was contained and this nickel was contacted on the skin of the body, fear, such as starting carcinogenic and allergy, is pointed out and these supercooling metals were not able to be used for accessories.
[0010] Furthermore, the conventional supercooling metal had many which carried out abundant content of the noble metals, and was not satisfactory as accessories from the point of asset value.
[0011]
[Problem(s) to be Solved by the Invention] This invention solves the above troubles, and hardness is hard, and it excels in gloss, and has the property in which workability is still larger, noble metals are contained so much, and it aims at offering an alloy suitable as a charge of accessories material that nickel is not included.
[0012]
[Means for Solving the Problem] this invention persons are P centering on a noble-metals ingredient apart from the above-mentioned conditions, as a result of carrying out various examination of the phenomenon in the above-mentioned supercooling metal. The compound of the low melting point was made in the alloy, and as a result of inquiring wholeheartedly focusing on the combination of an alloy with the eutectic point, it succeeded in finding out BARUKUAMORUFASU with Pt group system ingredient.

[0013] It is the alloy which consists of Pt-Pd-Cu-P, the percentage of each component is 5 <=Pt<=70at% and 5 <=Pd<=50at% and 5 <=Cu<=50at% and 5 <=P <=30at%, and the invention in this application for solving the above-mentioned technical problem is further, after this alloy's dissolving. It is the supercooling metal for ornament ingredients characterized by being cooled by 101 degree-C/sec- 102 degree C/sec.
[0014] Even if the alloy for supercooling metals of the above-mentioned configuration carries out quenching carried out comparatively slowly after the dissolution, it will be in a supercooling condition easily and will have the property that hardness is hard. Since this supercooling metal is glossy and does not contain nickel component at all further, including noble metals so much, it is very more useful still as a charge of ornament material.
[0015] It will crystallize, if it becomes a supercooling metal and shifts from this range also of one component, when each component has balanced 4 yuan by said density range as a system alloy, and it stops becoming a supercooling metal.
[0016] When making it into a final product by casting, the supercooling metal of this invention remains as it is, and serves as a product with hard hardness. Furthermore, when machining, even if it can perform cutting in ordinary temperature, plastic working is too hard and it is hard to process it, but if it heats between glass transition-temperature - crystallization temperature, super-elasticity will be shown and it will become easy to process it.
[0017]
[Embodiment of the Invention] If each component is mixed by said density range, it can be manufactured, but as for the supercooling metal of this invention, it is desirable to use a powdered metal in order to bring the dissolution forward.
[0018] Moreover, Cu component is P although you may add as a pure metal. A phosphor copper compound (Cu3P grade) may be used for concentration preparation. Moreover, it is desirable to add borax etc. for the purpose of antioxidizing. In addition, it is desirable to carry out in inert atmospheres, such as Ar gas, and after melting is good to carry out bubbling of the Ar gas etc. to degasifying to serve both as churning.
[0019] Although quenching after the dissolution does not ask especially an approach, it should just perform quenching of 101 degrees C/sec - 102 degrees C / sec extent. It can attain by soaking underwater as an easy approach the whole end crater in which a quartz tube etc. is.
It investigated whether the rate of <example 1> constituent concentration is changed, various kinds of alloys would be produced, and it would quench after the dissolution, and would become a supercooling metal (does it vitrify?).
[0020] the shape of powdered red phosphorus and a pellet -- Cu3P, Pt powder, and Pd powder were mixed so that 100g and the rate of each component might become as it is shown in Table 1 in total, what added 5g of borax further was put into the ****** quartz tube of bore 20phi, and heating was started with the electric furnace of Ar ambient atmosphere. It heated to 1100 degrees C, and after the dissolution, it served both as stirring and degasifying and bubbling of the Ar gas was carried out for 1 minute into the molten metal. Then, the dissolved metal was soaked underwater the whole quartz tube, and was quenched. The quartz tube after cooling was broken and the sample was started by the high cutter. Whenever [vitrification / of a sample] was investigated by applying this sample to differential thermal analysis, and measuring that glass transition temperature and crystallization temperature. Furthermore, the Vickers hardness number of a sample was also measured. Those results are shown in Table 1.
[0021]
[Table 1]

No.	成分割合 (at%)				ガラス化度 (注1)	ビッカース硬さ (H_v)
	Pt	Pd	Cu	P		
1	10	30	40	20	○	490
2	10	40	30	20	◎	480
3	10	50	20	20	○	500
4	10	60	10	20	×	600
5	20	20	40	20	○	510
6	20	30	30	20	◎	470
7	20	40	20	20	◎	460
8	20	50	10	20	×	590
9	30	10	40	20	○	510
10	30	20	30	20	◎	450
11	30	30	20	20	◎	450
12	30	40	10	20	○	500
13	39	2	39	20	×	580
14	40	10	30	20	○	510
15	40	20	20	20	◎	460
16	40	30	10	20	○	500
17	39	39	2	20	×	580
18	2.5	40	37.5	20	×	590
19	5	40	35	20	○	520
20	7.5	40	32.5	20	○	530
21	25	30	25	20	◎	470
22	21	26	21	32	×	590
23	23	29	23	25	○	520
24	27	31	27	15	○	510
25	29	34	29	8	×	600
26	50	10	20	20	○	530
27	50	20	10	20	○	490
28	60	10	10	20	○	520
29	65	5	10	20	○	500
30	70	5	5	20	○	510

注1：ガラス化度

◎－完全にガラス化，○－表面はガラス化，×－結晶化

[0022] Thus, as for the alloy of this invention, whenever [vitrification] becomes high comparatively easily, and what has hard hardness is obtained. Moreover, all the supercooling metals of this invention were excellent also in gloss. No.11 among the supercooling metals obtained in the <example 2> example 1 It machined further about the sample. No.11 ****** -- glass transition temperature TG 289 ** and crystallization temperature TX the place which heated the rod-like sample to 300 **, and was pulled with both ends although it was 348 degrees C, and it is weak and was hard to carry out plastic working in ordinary temperature -- very much -- good -- elongation -- it became a thin line.

[0023]

[Effect of the Invention] As mentioned above, the alloy for supercooling metals for the ornament ingredient of this invention can make a supercooling metal easily, and is very useful as a charge of ornament material.

[0024] Moreover, since are hard to attach a crack, and it is rich also in glossiness, and is processible and nickel is not further included even if the supercooling metal for ornament ingredients of this invention has hard hardness and it receives friction, it has many descriptions -- there are no worries about carcinogenic [resulting from this element] or allergy -- and when it uses for accessories, the property which was very excellent is demonstrated.

[Translation done.]

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(54)【発明の名称】　装飾材料用過冷金属及び過冷金属用合金

(57)【要約】
【課題】　硬さが硬く、光沢性及び加工性に優れ、さらに人体への影響の無い装飾用材料を提供する。
【解決手段】　Pt-Pd-Cu-Pより成り、各成分の割合が５≦Pt≦70at%，５≦Pd≦50at%，５≦Cu≦50at%及び５≦P ≦30at%である合金であり、上記合金が溶解後 10^{1}℃/sec～ 10^{2}℃/secで冷却されていることを特徴とする装飾材料用過冷金属。

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【特許請求の範囲】

【請求項1】 Pt-Pd-Cu-Pより成る合金で、各成分の割合が5≦Pt≦70at%，5≦Pd≦50at%，5≦Cu≦50at%及び5≦P ≦30at%であり、さらに該合金が溶解後 10^1℃/sec～ 10^2℃/secで冷却されていることを特徴とする装飾材料用過冷金属。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】装飾品に用いたときに最適な硬さがあり、さらに人体への影響の無いPt系合金材料に関する。

【0002】

【従来の技術】過冷金属は金属を溶融状態から急冷することにより得られるものであり、結晶化していないため硬さが硬い等、特異な性質を示す材料として近年注目されている。

【0003】これまで一般的に過冷金属を作るには急冷することが必須条件として考えられてきた。例えば、溶湯を高速回転する銅製の水冷ロールの上に落下させて薄い箔状テープやフレークにして過冷金属が作られてきている。

【0004】最近、このようにして作られる過冷金属合金の他に、バルクアモルファスと呼ばれる、箔でないインゴット状（鋳塊状）の過冷金属ができることがわかってきた。

【0005】冷却速度を速くすることは、形状が大きくなると表面と内部の冷却速度が変わり、表面は過冷金属となるが内部は通常の金属結晶をもつことになってしまう。従って、これまで速く冷却するには、薄い箔状のものしか作ることができなかった。

【0006】ところが、最近になって、比較的大きなインゴット状（鋳塊状）の過冷金属が比較的遅い冷却速度でありながら、ある種の合金組成で可能であることがわかってきた。

【0007】しかしながら、これらの合金元素の組成の組合せが、何故、過冷金属になるのかという理論的解析は未だ不明な点が多い。現象的にいくつかのこと（例えば、原子間距離の離れたもの同士の合金であることや、P 化合物を作るものとかいった現象）が挙げられているが、必ずしもそれが絶対的支配条件として成立するものではない。

【0008】ところでペンダント、指輪、ブローチ、ネックレス等の装飾品用材料や、歯科、カテーテル等の医療用材料として従来Au、Pt等の貴金属が用いられているが、これらの貴金属は軟らかいため、使用時の摩擦によりキズがつきやすいといった問題があった。この問題を解決するため、AuやPtといった貴金属に他の金属を少量添加して合金とすることにより硬さを増す方法が一般的に用いられているが、このような合金としても、硬さ等の点で充分満足がゆくものではなかった。

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【0009】また、このような装飾品の材料として前記のような過冷金属を用いるという考えも上がってきたが、最近報告されているインゴット状（鋳塊状）の過冷金属はそのほとんどが成分としてNiを含有しており、このNiを人体の皮膚と接触させた場合、発癌性やアレルギーを起こす等の恐れが指摘されており、これらの過冷金属を装飾品に用いることはできなかった。

【0010】さらに、従来の過冷金属は貴金属を多量含有したものが少なく、資産価値の点からも装飾品としては満足のゆくものではなかった。

【0011】

【発明が解決しようとする課題】本発明は上記のような問題点を解決し、硬さが硬く、光沢に優れ、さらに加工性が大きいといった性質を有し、貴金属を多量に含有し、Niを含まないといった、装飾品用材料として好適な合金を提供することを目的とする。

【0012】

【課題を解決するための手段】本発明者らは、上記過冷金属における現象を各種検討した結果、上記の条件とは別に貴金属材料を中心として、P との合金において低融点の化合物を作り、共晶点をもつ合金の組合せを中心に鋭意研究した結果、Pt族系材料でバルクアモルファスを見出すことに成功した。

【0013】上記課題を解決するための本願発明は、Pt-Pd-Cu-Pより成る合金で、各成分の割合が5≦Pt≦70at%，5≦Pd≦50at%，5≦Cu≦50at%及び5≦P ≦30at%であり、さらに該合金が溶解後 10^1℃/sec～ 10^2℃/secで冷却されていることを特徴とする装飾材料用過冷金属である。

【0014】上記の構成の過冷金属用合金は、溶解後比較的ゆっくりした急冷をしても、容易に過冷状態となり、硬さが硬いといった特性を有する。さらにこの過冷金属は光沢性もあり、貴金属も多量に含み、さらにNi成分を全く含まないため、装飾用材料として非常に有用である。

【0015】4元系合金として、各成分が前記濃度範囲でバランスがとれていることにより過冷金属となるものであり、一成分でもこの範囲よりずれると結晶化してしまい、過冷金属にならなくなる。

【0016】本発明の過冷金属は、鋳造により最終製品とする場合、そのままで硬さの硬い製品となる。さらに、機械加工を施した場合、常温での切削はできても塑性加工は硬過ぎて加工しにくいが、ガラス遷移温度～結晶化温度の間に加熱すると、超塑性を示し、加工しやすくなる。

【0017】

【発明の実施の形態】本発明の過冷金属は、前記濃度範囲で各成分を混ぜれば製造可能であるが、溶解を早めるため粉末状金属を用いるのが好ましい。

【0018】また、Cu成分は、純金属として加えても良

いが、P の濃度調製のため、リン銅化合物（Cu_3P等）を用いても良い。また、酸化防止の目的のため硼砂等を加えることが好ましい。なお、Arガス等の不活性雰囲気中で行うのが好ましく、溶融後は脱ガスと撹拌を兼ねてArガス等をバブリングさせると良い。

【００１９】溶解後の急冷は、特に方法は問わないが、10^1℃/sec～10^2℃/sec程度の急冷を行えば良い。手軽な方法としては、石英管等のるつぼごと水中に漬けることにより達成できる。

＜実施例１＞成分濃度の割合を変えて各種の合金を作製し、溶解後急冷して過冷金属となるか（ガラス化するか）調査した。

【００２０】粉末状赤リン、小塊状Cu_3P、Pt粉末及びPd＊粉末を合計で100g、各成分の割合が表１のようになるように混合し、さらに硼砂5gを加えたものを内径20φの片封じ石英管に入れ、Ar雰囲気の電気炉にて加熱を開始した。1100℃まで加熱して溶解後、撹拌と脱ガスを兼ね溶湯中にArガスを１分間バブリングした。その後、溶解した金属を石英管ごと水中に漬けて急冷した。冷却後石英管を割り、試料をハイカッターで切り出した。この試料を示差熱分析にかけ、そのガラス遷移温度及び結晶化温度を測定することにより、試料のガラス化度を調べた。さらに、試料のビッカース硬さも測定した。それらの結果を表１に示す。

【００２１】

【表１】

No.	成分割合（at%）				ガラス化度（注1）	ビッカース硬さ（H_v）
	Pt	Pd	Cu	P		
1	10	30	40	20	○	490
2	10	40	30	20	◎	480
3	10	50	20	20	○	500
4	10	60	10	20	×	600
5	20	20	40	20	○	510
6	20	30	30	20	◎	470
7	20	40	20	20	◎	460
8	20	50	10	20	×	580
9	30	10	40	20	○	510
10	30	20	30	20	◎	450
11	30	30	20	20	◎	450
12	30	40	10	20	○	500
13	39	2	39	20	×	580
14	40	10	30	20	○	510
15	40	20	20	20	◎	460
16	40	30	10	20	○	500
17	39	39	2	20	×	580
18	2.5	40	37.5	20	×	590
19	5	40	35	20	○	520
20	7.5	40	32.5	20	○	530
21	25	30	25	20	◎	470
22	21	26	21	32	×	590
23	23	29	23	25	○	520
24	27	31	27	15	○	510
25	29	34	29	8	×	600
26	50	10	20	20	○	530
27	50	20	10	20	○	490
28	60	10	10	20	○	520
29	65	5	10	20	○	500
30	70	5	5	20	○	510

注１：ガラス化度

◎－完全にガラス化，○－表面はガラス化，×－結晶化

【００２２】このように本発明の合金は、比較的容易にガラス化度が高くなり、硬さの硬いものが得られている。また、本発明の過冷金属はすべて光沢も優れていた。

＜実施例２＞実施例１で得られた過冷金属のうち、No.11 の試料についてさらに機械加工を行った。No.11 の試料は、ガラス遷移温度T_G が289 ℃、結晶化温度T_X が348℃であり、常温ではもろく、塑性加工しにくいものであったが、棒状の試料を300 ℃に加熱し、両端を持って引っ張ったところ、非常に良く伸び細い線状となった。

【００２３】

【発明の効果】以上のように本発明の装飾材料のための過冷金属用合金は、容易に過冷金属を作ることができ、装飾用材料として大変有用なものである。

【００２４】また、本発明の装飾材料用過冷金属は、硬さが硬く、摩擦を受けてもキズがつきにくく、また光沢性にも富み、加工性もあり、さらにNiを含まないため、この元素に起因する発癌性やアレルギーの心配が無い等、多くの特徴を持ち、装飾品に用いたとき大変優れた性質を発揮するものである。